Catalyst Atoms Shown to Move During Reaction

A New Window into Nanoscale Chemistry

In a collaboration between the research groups of Miquel Salmeron and Gabor Somorjai, the nanoscale changes that catalysts undergo during a chemical reaction have been observed directly for the first time. By understanding more completely how a catalyst functions, smarter catalysts can be developed to, for example, fight pollution, feed hydrogen fuel cells, and produce fuel more efficiently.

Catalysts speed up the rates of chemical reactions and are essential to the production of many industrially important chemicals. They also play an important role in environmental chemistry, most famously exemplified by automobile catalytic converters. For decades, researchers have tried to better understand how catalysts work so that their functionality can be improved. This is challenging, as catalysts operate at the molecular scale. Moreover, it is known that they often change their structure during a chemical reaction, but, until now, there was no way to observe this directly.

Somorjai and Salmeron worked together to address this challenge. Using techniques developed in his lab, Somorjai synthesized bimetallic nanoscale particles composed of common catalytic metals such as rhodium and palladium, or platinum and palladium. Next, they used a unique photoelectron spectrometer developed by Salmeron and colleagues at the Advanced Light Source, Beamline 9.3.2 to identify elements and their chemical state. Unlike similar spectrometers, this instrument can be operated at the pressures and environments at which catalysts are normally used, instead of for example, high vacuum.

Using this system, the restructuring of the bimetallic nanoparticles as they were exposed to gases such as nitrogen oxide, carbon monoxide, and hydrogen could be seen directly. For example, in the presence of some reactants, rhodium atoms migrated to a particle's surface while in the presence of other reactants, the palladium atoms that migrated to the surface. By observing which metal segregates to the catalyst's surface and the chemical changes it undergoes, it can be seen which component of the catalyst drives the chemical reaction.

Now that it is possible to watch catalysts change in real time, new "smart" catalysts can be designed by ensuring that the most active metal is on the surface precisely when it is needed most. For example, researchers could engineer bimetallic nanoparticle catalysts in which one migrates to the surface during an initial stage of a reaction, and a different metal migrates to the surface in a latter stage. Such new catalysts could function far more specifically, the hallmark of "green chemistry," so that waste byproducts are minimized.

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Feng Tao, Michael E. Grass, Yawen Zhang, Derek R. Butcher, James R. Renzas, Zhi Liu, Jen Y. Chung, Bongjin S. Mun, Miquel Salmeron, Gabor A. Somorjai1, "Reaction-Driven Restructuring of Rh-Pd and Pt-Pd Core-Shell Nanoparticles." *Science* **322**, 932 (2008);

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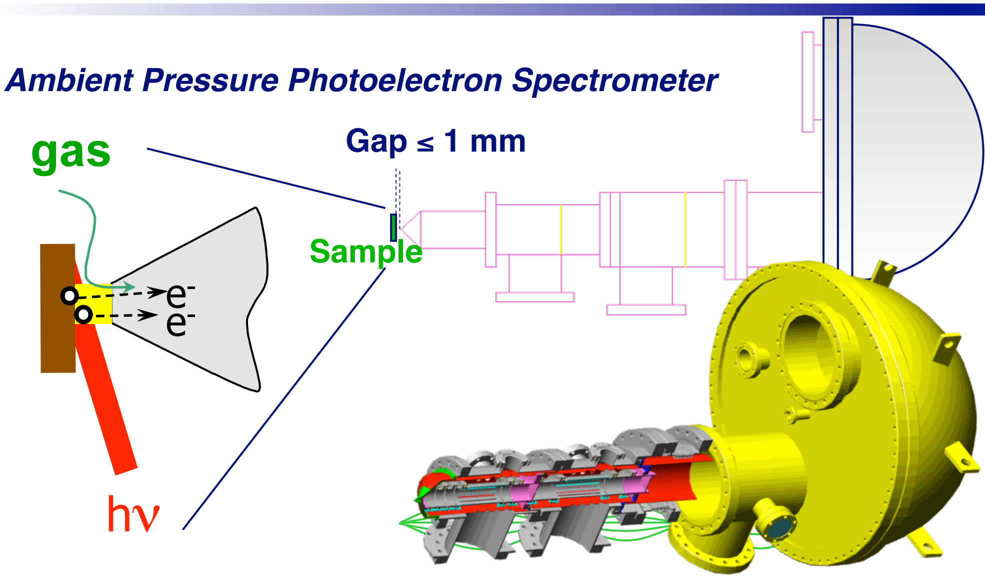
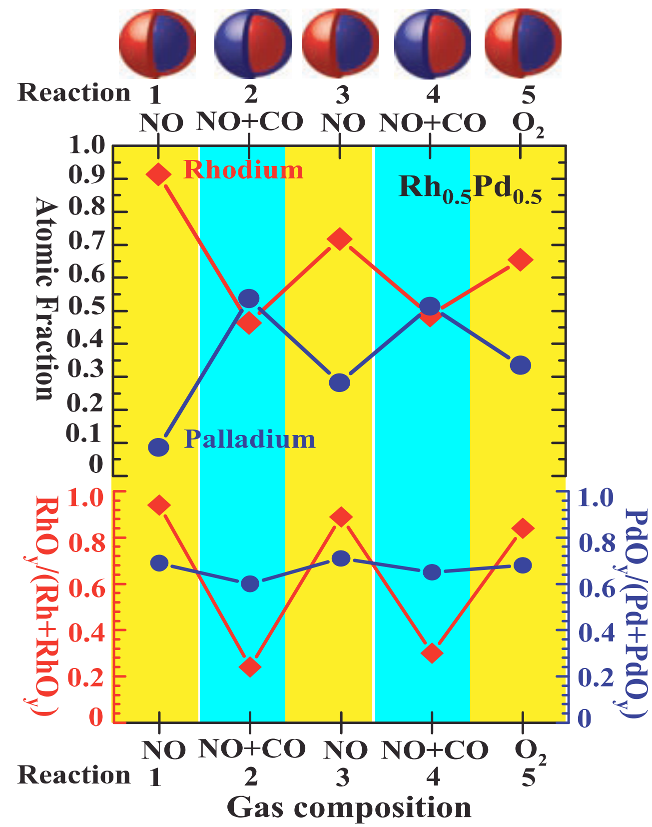
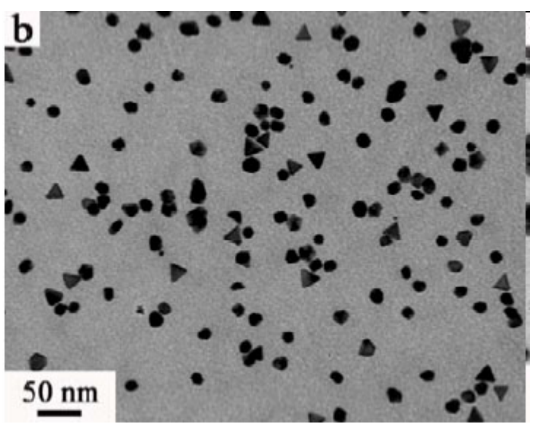
Ambient Pressure Photoelectron Spectrometer





High pressure photoelectron spectroscopy reveals directly the restructuring of the bimetallic catalysts during reactions*. Data for Rh-Pd nanoparticles is shown. Under oxidizing conditions (an NO or O_2 atmosphere, yellow shading) Rh atoms migrate to the surface (top graph) and are oxidized (lower graph). Under reaction conditions (NO + CO atmosphere, blue shading), Pd atoms migrate to the surface, and the fraction of oxidized Rh is reduced.*



Transmission electron microscopy *images of active bimetallic catalysts rhodium-palladium nanoparticles (top) and platinum-palladium nanoparticles (bottom).*